Stevens Inst. of Tech
NsG-494

The Pressure Dependence of Retention Volumes

F. B. Clough

This article reopens the question of how to use the net retention volumes of substances in gas-liquid chromatography to calculate their activity coefficients in the liquids which serve as stationary phase. The standard state for the solute is chosen to be the pure liquid solute under its own vapor.

Some[1] have adopted the pure liquid at zero pressure as standard state. This seems undesirable, since it involves the quantity $\int_{p^o}^{o} v^o dp$, which can only be evaluated if the molar volume of the pure solute, $\bar{v}^o$ is known as $p \to 0$. For volatile liquids this quantity is impossible to measure and in practice the integral is arbitrarily set equal to $(-v^o p^o)$. In treating free energies of mixing, it is customary to refer to the pure liquid under its own vapor,[2] so that Raoult's law gives $\mu - \mu^o = RT\ln X$. Otherwise, for another standard pressure p', $\mu - \mu' = RT\ln X + \int_{p'}^{p^o} v^o dp$.

Rowlinson[2] has pointed out that the uncertainty in the value of $\int vdp$ makes the concept of excess free energies of mixing (and activity coefficients) inapplicable when pressures of more than about 3 atmospheres are involved. We encounter a similar consideration in our analysis of the exact evaluation of activity coefficients from GLC data, and we arrive at an expression for the pressure dependence of retention volumes which is different from that of Everett.[1] The disagreement arises from the different choice of standard states and the approximations involved in evaluation of $\int vdp$, and it seems impossible to judge the relative merits of

pages 4
CR 84755
code none

N67-83992

the two expressions by purely thermodynamic arguments. The pressure dependence is small, but the issue becomes important if one hopes to use the observed pressure dependence to evaluate second virial coefficients of the carrier gas, or interaction virial coefficients.

We shall let (KV_L) represent the experimental quantity in the following discussion, although it is of course V_R^o and V_M which are directly observed. The familiar expression relating net retention volume and the partition coefficient is

(eq 1) $V_R^o - V_M = \frac{n_1}{n_{1(g)}} \cdot V_G = KV_L$. The activity coefficient is defined by $\mu_1 - \mu_1^o = RT\ln\gamma X_1$, where γ is a constant at any given pressure for sufficiently small mole fractions, and $\gamma \to 1$ for $X \to 1$ under pressure equal to the vapor pressure, p^o, of pure liquid solute.

The thermodynamic treatments all rest on the assumption that the flow through the column is sufficiently slow to permit thermodynamic equilibrium to be established at each point in the column (but not so slow that backward diffusion is significant). Consequently, chemical potentials are equal in the stationary and gas phase. For the solute in the vapor phase, it is customary to use a standard state different from that used for the liquid --

(eq 2) referring the vapor chemical potential to zero pressure: $\mu_{vap} = \mu_1^* + RT\ln \frac{f_1}{f^*}$

f is the fugacity, with $f^* = 1$. Consequently, at equilibrium in the column,

(eq 3) $\mu_1 - \mu_1^o = RT\ln\gamma X_1 = \mu_1^* + RT\ln f_1 - \mu_1^o$. f_1 of course is the fugacity of the solute in the vapor when the total pressure is the column pressure, P. We can evaluate the left hand expression by considering the changes in chemical potential through the following succession of states from the solute:

1) Standard State ($\mu = \mu^o$, $\gamma = 1$, $p = p_1^o$).

2) Reference State (liquid) - pure liquid under column pressure $\bar{p} = p_1^{o(ref)} + p_3$.

3) Reference State (vapor) - $p_1^{o(ref)} = X^o_{1(g)}\,\bar{p}$

4) Gas mixture at low pressure p^* ($p_1^* = X^o_{1(g)}p^*$)

5) Gas mixture at pressure p^*, but diluted with carrier gas so that mole fraction of solute = $X_{1(g)}$. This is the composition of the vapor at equilibrium at some point in the column.

6) Gas mixture with composition $X_{1(g)}$ at pressure $\bar{p}$.

7) Solute in liquid phase on column, in equilibrium with vapor of composition $X_{1(g)}$. (In liquid phase, mole fraction of solute = X_1)

The changes in chemical potential are:

$$\Delta\mu_{1-2} = \mu_{ref} - \mu^o = \int_{p^o}^{\bar{p}} V^o dp = V^o(\bar{p} - p^o)$$

$$\Delta\mu_{2-3} = 0$$

$$\Delta\mu_{3-4} = RT\ln p_1^* - RT\ln f_1^{o(ref)} = RT\ln \frac{X^o_{1(g)}p^*}{f_1^{o(ref)}}$$

$$\Delta\mu_{4-5} = RT\ln \frac{X_{1(g)}}{X^o_{1(g)}}$$

$$\Delta\mu_{5-6} = RT\ln f_1 - RT\ln p^*X_{1(g)} = RT\ln \frac{f_1}{p^*X_{1(g)}}$$

$$\Delta\mu_{6-7} = 0$$

Summing these -- $\mu - \mu^o = V^o(\bar{p}-p^o) + RT\ln \dfrac{f_1}{f_1^{o(ref)}}$

(eq 4) $$\ln\gamma = \ln \frac{f_1}{X_1 f_1^{o(ref)}} + \frac{V^o}{RT}(\bar{p}-p^o)$$

There are two fugacities to evaluate in this expression, one for the very dilute solute in the column vapor at composition $X_{1(g)}$, the other for the solute in the reference state at the much larger composition $X^{o}_{1(g)}$. The customary expression for fugacities in terms of second virial coefficients can be applied to each[3]

(eq 5) $$\ln \frac{f_1}{f_1^{o(ref)}} = \ln p_1 - \ln p_1^{o(ref)} + \frac{\bar{p}}{RT}\left((Y_3^o)^2 - y_3^2\right)(B_{33} - 2B_{13} + B_{11})$$

The distinction between $p_1^{o(ref)}$ and the vapor pressure p_1^o can be ignored. Also $p_1 = X_{1(g)}\,\bar{p}$. Then, from eq (4),

(eq 6) $$\ln\gamma = \ln \frac{X_{1(g)}\,\bar{p}}{X_1\,p_1^o} + \frac{V^o}{RT}(\bar{p} - p^o) + \frac{\bar{p}}{RT}\left((Y_3^o)^2 - y_3^2\right)(B_{33} - 2B_{13} + B_{11})$$

To introduce the experimental property, KV_L, Everett's[1] approach can be used. The thermodynamic theory of the column indicates that the limiting value of $\frac{X_{1(g)}}{X_1}$ applies (Henry's law constant), and the activity coefficients determined by GLC are for the solute at infinite dilution. By definition $KV_L = \frac{n_{1(L)}}{n_{1(g)}} V_G = \frac{X_1\, n^s\, V_g'}{X_{1(g)} n_g}$, $n^s = \frac{W_s}{M_s}$, the number of moles of stationary liquid (solvent) in the column. $\frac{V_g'}{n_g}$ is the molar volume of gas phase, and since it is almost pure carrier gas, we can use the virial expansion: $\frac{V_g''}{n_g} = \frac{RT}{P} + B_{33}$. Consequently $KV_L = \lim_{X_1 \to 0} \frac{X_1}{X_{1(g)}} \left(\frac{RT}{P} + B_{33}\right)$

Therefore $\lim_{X\to 0} \dfrac{X_{1(g)}p\bar{p}}{X_1\, p_1^o} = \dfrac{RT}{(KV_L)}\,\dfrac{n^s}{p_1^o}\,[\,1 + \dfrac{B_{33}\,\bar{p}}{RT}\,]$

and $\lim_{X\to 0} \ln \dfrac{X_{1(g)}\,\bar{p}}{X_1\, p_1^o} \simeq \ln\left[\dfrac{RT}{(KV_L)}\;\dfrac{n^s}{p_1^o}\right] + \dfrac{B_{33}\,\bar{p}}{RT}$.

The term $[\,(Y^o)^2 - Y^2\,]$ can be replaced by $\left(\dfrac{\bar{p} - p_1^o}{\bar{p}}\right)^2 - 1 =$

$\dfrac{(\,\bar{p} - p_1^o\,)^2 - \bar{p}^2}{\bar{p}^{\,2}} = \dfrac{(p_1^o)^2 - 2\,p_1^o\,\bar{p}}{\bar{p}^{\,2}}$, since Y^o is the mole fraction of carrier gas in the vapor at pressure $\bar{p}$ in the reference state (state 3). Y, the composition of gas in the column, is almost 1.

Finally, we must choose a pressure, 1 atm, to evaluate $\ln\gamma$. $\ln\gamma_{1\ atm} = \ln\gamma_{(p)} - \dfrac{\bar{V}_1}{RT}(\bar{p} - 1)$, taking the partial molar volume $\bar{V}_1$ of solute in the stationary phase to be independent of pressure.

Making these substitutions into (eq 6), we arrive at an equation for $\ln\gamma_{1\ atm}$

$$\ln\gamma_{1\ atm} = \ln \frac{RT\,W_s}{p_1^o\,M_s} - \ln(KV_L) - \frac{V^o\,p^o}{RT} - \frac{2\,p_1^o}{}\,(\,B_{11} - 2\,B_{13} + B_{33}\,) + \frac{\bar{V}_1}{RT}$$

(eq 7a)

$$+ \frac{(\,B_{33} + V^o - \bar{V}_1)}{RT}\,\bar{p} + \frac{(p_1^o)^2}{\bar{p}RT}\,(\,B_{11} - 2\,B_{13} + B_{33}\,)$$

Alternatively, the pressure dependence of (KV_L) (i.e., of the experimental net retention volumes) is

$$\ln(KV_L) = ([-\ln\gamma_{1\ atm} + \ln \frac{RT\ W_s}{p_1^o\ M_s} + \frac{1}{RT} (\bar{V}_1 - V^o\ p^c) - [\text{illegible}] ([\text{illegible}] - [\text{illegible}]_3$$

$$+ \frac{B_{33} + V^o - \bar{V}_1}{RT}\ \bar{p} + \frac{1}{\bar{p}}\ \frac{(p_1^o)^2}{RT} (B_{11} - 2\ B_{13} + B_{33}$$

$$= C + B\,\bar{p} + \frac{A}{\bar{p}}$$

References

1. D. H. Everett, Trans. Far. Soc., 61, 1637 (1965).

2. Rowlinson, Liquids and Liquid Mixtures (Butterworth, 19[illegible]) [illegible]

3. Guggenheim, Thermodynamics (3rd ed., North Holland, 1957).